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Liquid–liquid equilibria and thermo physical properties for 1-methyl-2-pyrrolidinone + heterocyclic nitrogen compounds + hexadecane systems at 298.15 K

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ABSTRACT

Liquid–liquid equilibrium data for {1-methyl-2-pyrrolidinone (NMP) + heterocyclic nitrogen compounds + hexadecane} systems were analytically determined at 298.15 K and atmospheric pressure using stirred and thermo-regulated cell. The experimental data were modeled with the NRTL and UNIQUAC equations. Besides, the Bachman–Brown correlation was used to ascertain the reliability of the experimental data. Additionally, excess molar volumes (V^E) and deviations in the molar refractivity (ΔR) data at 298.15 K were determined for the {NMP + heterocyclic nitrogen compounds} binary systems using a digital vibrating-tube densimeter and a precision digital refractometer. The V^E and ΔR data were modeled with the Redlich–Kister equation.

1. Introduction

In recent years, the rising cost of energy has made new separation processes based on extraction more attractive than before because solvent extraction only requires different solubilities of compounds in two immiscible liquid phases. Therefore, liquid extraction provides an important alternative to distillation in the production of fine organic compounds, nuclear reprocessing, ore processing, production of perfumes and many other industries. Air pollution caused by diesel exhaust gas has received much attention, and to protect the environment against contamination, the sulfur-limit in diesel fuel was regulated to a maximum of 15 ppm in the USA by 2010 and to 10 ppm in Europe by 2009. However, many fuel producers have difficulty meeting these new specifications for ultra-low-sulfur diesel (ULSD) from both a technical and economical perspective.

Hydrodesulfurization (HDS) is the most commonly used process in the oil industry to reduce the sulfur content in diesel fuel and converts sulfur compounds into hydrogen sulfide [1–4]. Refinery HDS feedstocks (naphtha, kerosene, diesel oil and heavier oils) contain a wide range of organic sulfur compounds, e.g., thiols, thiophenes, organic sulfides and disulfidesc. Therefore, removal of these sulfur compounds may require very severe operating conditions to achieve the sulfur-limit for ULSD with the conventional HDS process. Recently, reports have indicated that conventional HDS processes can be successfully applied in ULSD production if heterocyclic nitrogen-containing compounds are removed from the HDS feedstock. This removal is necessary because they act as an inhibitor of the desulfurization process in the middle distillates.

We systematically report the phase equilibria and mixture properties for several nitrogen-containing compounds because accurate data for such properties are critical when designing the extraction process for nitrogen-containing compounds from the middle distillate [5–7].

In this work, we report liquid–liquid equilibrium (LLE) data for ternary systems {1-methyl-2-pyrrolidinone (NMP) + heterocyclic nitrogen compounds (quinoline, pyridine, pyrrole, aniline) + hexadecane} at 298.15 K and atmospheric pressure. NMP was selected as the extractive solvent for nitrogen compounds because it is a dipolar aprotic solvent, like dimethylformamide, which is used as a solvent for nitrogen compounds. Hexadecane was chosen as a model compound for diesel oil. The experimental LLE data for the ternary systems were modeled using two activity coefficient models: NRTL [8] and UNIQUAC [9].

In addition, excess molar volumes (V^E) and deviations in the molar refractivity (ΔR) data at 298.15 K were determined for binary systems {NMP + heterocyclic nitrogen compounds (quinoline, pyridine, pyrrole, aniline)} using a digital vibrating-tube densimeter and a precision digital refractometer. The V^E and ΔR data were modeled with the Redlich–Kister [10] equation.

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Nomenclature

List of symbols

A_i	adjustable parameter for the Redlich–Kister and Cibulka's equation
A, B	Bachman–Brown correlation parameters
M_i	molar mass of the pure component i (g mol^{-1})
N	number of experimental data points
n	number of parameters A
n_D	refractive indices
OF	objective function
q	UNIQUAC parameter
RMSD	root mean square deviation
ΔR	deviations in molar refractivity (cm^3 mol^{-1})
r	UNIQUAC parameter
V^E	excess molar volume (cm^3 mol^{-1})
x	mole fraction

Superscripts

Exp	experimental value
Cal	calculated value
α	phase α

Subscripts

i	component i
k	tie-line k

Greek letters

ρ_i	density of component i (g cm^{-3})
ρ_m	density of the mixture (g cm^{-3})
σ_{st}	standard deviation
ϕ_i	volume fraction of the pure component in the mixture

2. Experimental

2.1. Chemicals

Commercial, analytical-grade chemicals were used in this investigation. NMP (C_5H_9NO, $M = 99.13$ g mol^{-1}, CAS-RN 872-50-4, >99.9%), hexadecane ($C_{16}H_{34}O$, $M = 226.45$ g mol^{-1}, CAS-RN 544-76-3, >99.0%), pyridine (C_5H_5O, $M = 79.10$ g mol^{-1}, CAS-RN 110-86-1, >99.0%), and aniline (C_6H_7N, $M = 93.13$ g mol^{-1}, CAS-RN 62-53-3, >99.0%) were obtained from Aldrich Co. Pyrrole (C_4H_5N, $M = 67.09$ g mol^{-1}, CAS-RN 109-97-7, >97.0%) was obtained from Fluka, and quinoline (C_9H_7N, $M = 129.16$ g mol^{-1}, CAS-RN 91-22-5, >99.0%) was obtained from Junsei Chemical Co. All chemicals were dried using molecular sieves with a pore diameter of 0.3 nm. The water content of the chemicals, determined using a Karl–Fischer titrator (Metrohm 684 KF-Coulometer), was less than 8×10^{-5} g g^{-1}. The purity of the chemicals was checked by gas chromatography and by comparing the densities with values reported in the literature [11–15]. The measured and reported values for the purities, densities and refractive indices of the chemicals are listed in Table 1.

2.2. Procedure

LLE measurements were carried out by determining the end points of the tie-lines for all of the ternary systems. The LLE determination apparatus in our laboratory is similar to that reported by Correa et al. [16]. It consists of three parts: an equilibrium glass vessel jacket, a thermostat (Lauda MD 20 with DLK15 cooler) with a system that precisely measures the temperature (A∑A F250), and a Corning PC-320 magnetic stirrer. The temperature of the liquid sample in the equilibrium vessel was regulated by the thermostat to within ±0.02 K of the set point. Fig. 1 shows the schematic diagram of this LLE measurement system. The sample mixture was stirred rigorously in the equilibrium vessel for about 4 h, and was then allowed to settle for more than 8 h at a constant temperature, allowing the upper and lower phases to reach phase equilibrium. After arriving at the equilibrium state for the two liquid phases, samples were carefully taken from the top for the upper liquid phase and from the bottom for the lower liquid phase without cross contamination during the sampling procedure. The sample analysis was performed using a gas chromatograph (HP 6890N) equipped with an HP-FFAP (polyethylene glycol TPA, 25 m × 0.20 mm × 0.30 μm) capillary column and a thermal conductivity detector. The chromatographic method involved an injection volume of 1 μl with a split ratio of 25:1. The injector and detector temperatures were set to 483.15 K and 493.15 K, respectively. The oven temperature was maintained at 333.15 K for 2.5 min and was then increased at a rate of 50 °C min^{-1} to reach the final temperature of 473.15 K, which was maintained for 6 min. The carrier gas was helium, and a flow rate of 2.0 ml s^{-1} was maintained throughout the column. The uncertainty of the calculated mole fractions was estimated to be less than $\pm 1 \times 10^{-4}$.

Densities were measured by a digital vibrating glass tube densimeter (Anton Paar, model DMA 5000, Graz, Austria). The uncertainty of the densimeter was stated to be 5×10^{-6} g cm^{-3} in the range of 0–3 g cm^{-3}. Temperature was controlled to ±0.01 K in the range from 273.15 K to 363.15 K. The details of the operating procedures have been described elsewhere [17,18]. Refractive indices

Table 1
Properties of used chemicals.

Chemicals	GC analysis (wt%)	ρ (g cm^{-3}) at 298.15 K		n_D at 298.15 K		UNIQUAC	
		This work	Reference[a]	This work	Reference	r-Value[a]	q-Value[a]
NMP	>99.7	1.02795	1.02790	1.46856	1.46750[c]	3.9810	3.2000
Hexadecane	>99.8	0.77323	0.77330	1.43260	1.43286[d]	11.2438	9.2560
Quinoline	>99.6	1.08939	1.09290[b]	–	–	4.7923	3.1530
Pyridine	>99.5	0.97815	0.97820	1.50715	1.51020[e]	2.9993	2.1130
Pyrrole	>99.0	0.96592	0.96980[b]	1.50761	1.50272[f]	2.5734	1.8240
Aniline	>99.6	1.01754	1.01750	1.58303	1.58630[e]	3.7165	2.8160

[a] Ref. [11].
[b] At 293.15 K.
[c] Ref. [12].
[d] Ref. [13].
[e] Ref. [14].
[f] Ref. [15].